REMOVAL AND RECOVERY OF NITROGEN AND SULFUR COMPOUNDS FROM COAL TAR FRACTIONS USING SUPPORTED ALMINIUM SULFATE UNDER SUPERCRITICAL CO_2 CONDITIONS

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ABSTRACT

Removal and recovery of nitrogen and sulfur compounds from coal tar fractions such as crude naphthalene and methylnaphthalene oils are examined using 10 wt% $Al_2(SO_4)_3/SiO_2$ as a solid acid under atmospheric or supercritical CO_2 (50℃, 80 atm) conditions. Repeated use of the solid acid is achieved by purging adsorbed nitrogen compounds with higher pressure (150 atm) CO_2 and methanol as an entrainer solvent, recovering effectively quinoline bases as well as purifying methylnaphthalenes.

Benzothiophene (BT) is dimerized over $Al_2(SO_4)_3/SiO_2$ catalyst under supercritical CO_2 conditions in order to separate BT from crude naphthalene as well as to purify naphthalene. BT was more selectively dimerized under supercritical CO_2 conditions(100℃, 100 atm) than in atmospheric n-octane solution at 100℃, allowing its selective dimerization and adsorption on the solid acid with selective extraction of naphthalene.

Effects of supercritical CO_2 conditions on the above adsorptions and reactions are discussed based on the analysis of recovered fractions and products.

INTRODUCTION

Crude methylnaphthalene oil(CMNO) is prepared as a residue of naphthalene oil (b.p. 210～260℃) of coal tar after the recovery of crude naphthalene.[1)] CMNO is further extracted with sulfuric acid and then neutralized with alkali to recover basic quinoline oil.[2,3)] However, because of the consumption of both acid and base as well as sludge formation, such a purification procedure appears no more feasible in the modern industry.[4)]

The present authors have reported that a consecutive solvent extraction with first methanol and then hexane concentrates the pyrroles and phenols in the hexane insoluble-methanol soluble fraction (HI-MS).[5)] Major basic nitrogen species staying in the methanol insoluble fraction(MI) are captured and recovered by adsorption and desorption, using nickel sulfate.[6-8)] The sulfate is known acidic and neutral, respectively, when it is dehydrated or rehydrated.[9)] High dispersion and proper heat-treatment of the sulfate increase the number and strength of acidic sites by supporting on silica gel for larger capacity against the adsorption of basic nitrogen compounds.[7,8)]

The present authors succeeded in removing nitrogen compounds from CMNO and recovering them in concentrated form using alminium sulfate on silica gel as the adsorbent.[10)] The supporting on silica gel disperses the sulfate on the surface, increasing the acidic strength and number of acidic sites. Hence, the surface which can get access to quinoline bases is essential as the support, larger pores being preferable. It was also reported that non-polar and poor solvents such as hexane and pentane appear to behave as an anti-solvent to expel the polar as well as basic compounds in methylnaphthalenes onto the adsorbent. Poorer solvents such as supercritical propane and carbon dioxide appear attractive.

In the present study, the removal and recovery of nitrogen compoumds in crude methyl-naphthalene oil (CMNO) obtained from coal tar were investigated using $Al_2(SO_4)_3$, more acidic than $NiSO_4$, supported on silica gel to obtain highly denitrogenated CMNO as well as to recover

basic quinoline bases under atmospheric or supercritical CO_2 conditions.

Crude naphthalene is commercially purified by hydrotreatments to remove nitrogen and sulfur compounds, however these heterocyclic compounds such as indole and benzothiophene could be used as valuable chemicals and medicines if they could be recovered. In the present study, recovery of benzothiophene(BT) was also examined using the $Al_2(SO_4)_3$ catalyst by designing the selective dimerization of BT with extraction of purified naphthalene followed by BT de-dimerization under the supercritical CO_2 conditions.

EXPERIMENTAL

Aluminium sulfate(10 wt%) was supported by impregnation from aqueous solution on silica gel of MB-4B provided by Fuji-Davison Chemical Ltd. The surface area and mean pore diameter of the silica gel were 500 m^2/g and 64 Å, respectively. The adsorbent was calcined at 350℃ for 4 h in air.

Model methylnaphthalene oil (quinoline:Q 8wt%, isoquinoline:IQ 8wt%, 1- and 2-methyl-naphthalenes: 1- and 2-MN 42wt% each) was prepared for the supercritical extraction experiments. Figure 1 shows the supercritical CO_2 extraction apparatus used in the present study. The model feed was charged to extraction vessel, and supercritical CO_2 (50℃, 80 atm) was flowed at 6 l/min to carry the feed to the fixed bed column filled with the $Al_2(SO_4)_3$ adsorbent. After the adsorbent was saturated with nitrogen compounds, higher pressure CO_2 and then methanol was flowed to recover the adsorbed species and to regenerate the adsorbent for its repeated use. The eluted and recovered fractions were analyzed and quantified by GC-FID (50 m capillary OV- 101 column, 110℃).

Benzothiophene(BT) in crude naphthalene was extracted and dimerized using several catalysts in atmospheric hexane and octane, respectively or supercritical CO_2 solvent at 100℃ for 3 h in order to separate BT from naphthalene. The fractionated and reaction products were analyzed by the elemental analysis, LC and FD-MS.

RESULTS AND DISCUSSIONS

Removal and Recovery of Quinolines from Model Methylnaphthalene Oil

Figure 2 shows the elution profile of the model methylnaphthalene oil using 10 wt% $Al_2(SO_4)_3$ /SiO_2 as an adsorbent in the fixed bed apparatus under supercritical CO_2 conditions. No nitrogen compounds were eluted until the extraction time of 120min, only denitrogenated methylnaphthalenes being recovered at the separation vessel. At the extraction time of 220 min when the adsorbed compounds were hardly extracted, CO_2 was pressurized upto 150 atm which was kept for 60 min to recover the adsorbates, and then methanol was added to CO_2 flow as an entrainer, almost all the adsorbed nitrogen compounds being desorbed and recovered from the adsorbent.

Figure 3 illustrates the elution curve of each compound in the model methlnaphthalene feed, where the elution conditions are same as Figure 2. 62% of methylnaphthalenes in the feed was recovered without nitrogen compounds, in other words, quinoline and isoquinoline were not eluted until about 60% of the feed was eluted. The activity of the adsorbent in the repeated adsorption/ desorption cycle is shown in Figure 4. The adsorption capacity of 10wt% $Al_2(SO_4)_3/SiO_2$ was restored to almost the same level of the first run in the second run by purging almost completely the remaining adsorbates which consist mainly of nitrogen compounds. The adsorption activity of the adsorbent was gradually decreased with the repetition number of the adsorption/desorption cycle, indicating that some deactivation of the adsorbent should take place during the adsorption/desorption repetition. More polar and/or dried entrainers may be very effective in achieving the complete recovery of nitrogen compounds without the deterioration of the adsorbent. Adsorbents should be designed in combination with eluting solvents for the completely reversible adsorption/ desorption performances.

Removal of Benzothiophene from Crude Naphthalene

Table 1 summarizes the adsorption treatment of crude naphthalene with various adsorbents in

atmospheric n-hexane solution followed by filtration to recover hexane-eluted fraction and washing of the adsorbent with benzene to recover adsorbed compounds. Sulfur as well as nitrogen compounds were removed from crude naphthalene, purified naphthalene and hetero-atom compounds being concentrated in haxane and benzene eluates, respectively, although the sulfur removal was not so effective as the nitrogen removal, because the basicity of sulfur compounds is not so strong as nitrogen compounds.

Recovery scheme of purified naphthalene(Np) and benzothiophene(BT) under supercritical CO_2 conditions is illustrated in Figure 5. BT is selectively dimerized and adsorbed on solid acid catalyst, naphthalene being purified and recovered by extraction with supercritical CO_2. BT dimer may be converted to BT monomer at a higher temperature, BT being recovered by supercritical CO_2 extraction. Figures 6 and 7 show the FD-MS spectra of the oligomerization products from the reaction of BT with 10wt% $Al_2(SO_4)_3/SiO_2$ catalyst at 100℃ for 3 h in atmospheric octane and supercritical CO_2 solvent, respectively. It is noted that BT is more selectively converted to its dimer in supercritical CO_2 solvent than in atmospheric octane solution, suggesting a remarkable solvent effect on the reactivity of BT and the selectivity to its dimer. Such a highly selective dimerization in supercritical CO_2 solvent was also observed in the oligomerization reaction of the mixture of BT and naphthalene under the same reaction conditions. More cross-oligomerization products between BT and naphthalene were produced in atmospheric octane solution at 100℃, suggesting that the supercritical CO_2 solvent may enhance the more preferable interaction of BT with the catalyst to that of naphthalene.

Reaction conditions including temperatures and pressures of dimerization and extraction, and catalyst should be further optimized to acieve more selective conversion to BT dimer and recovery of BT monomer after selective extraction of purified naphthalene.

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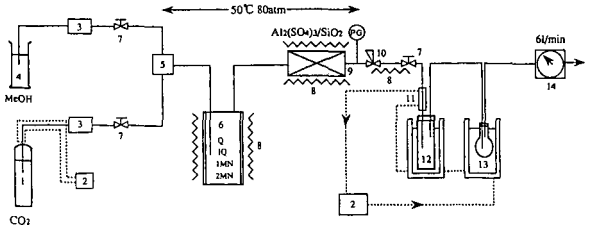

1. CO_2 cylinder	6. Extraction vessel	11. Liebig condenser
2. Cooler unit	7. Needle valve	12. Sampling vessel
3. Pressure pump	8. Heater	13. Trap
4. Entrainer reservoir	9. Packed column	14. Flow meter
5. Static mixer	10. Back pressure regulator	

Fig 1 Supercritical CO2 extraction apparatus

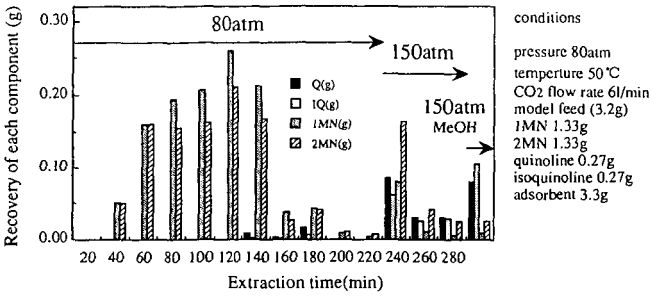

Fig2 Elution profile of model methylnaphthalene oil under supercritical CO_2 conditions

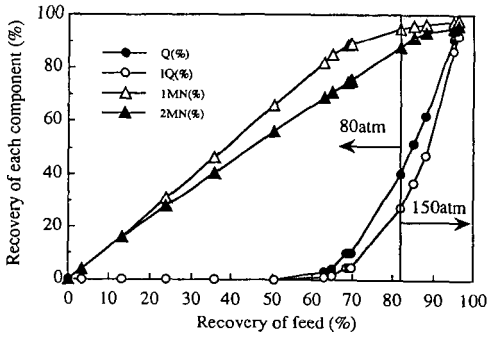

Fig3 Elution curve of each compound in the model methylnaphthalene oil under supercritical CO_2 extraction conditions (conditions;see Fig2)

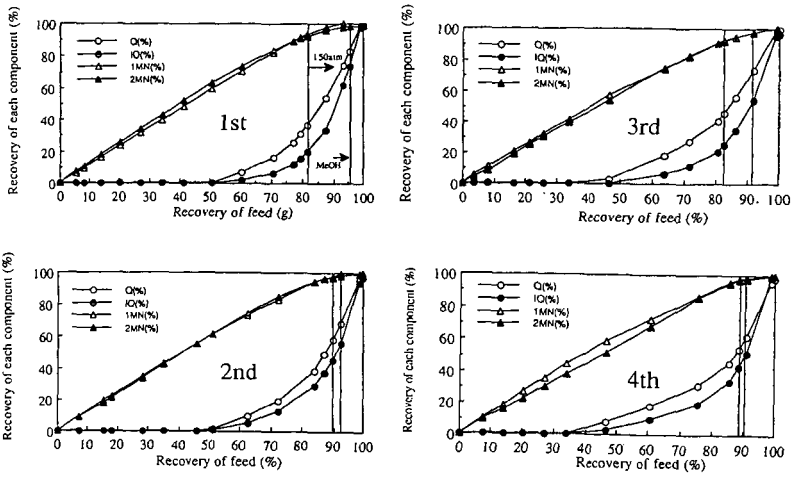

Fig 4 Repeated activity of the adsorbent for adsorption / desorption treatment of model methylnaphthalene oil under supercritical CO_2 conditions
(conditions; 50℃-80atm catalyst 2.3g)

Table 1 Adsorption treatment of crude naphthalene with various adsorbents in atmospheric hexane solution

Adsorbent	Eluting solvent	Recovery (wt%)	Elemental analysis S(%)	N(ppm)
Original crude naphthalene		—	1.6	500
10%$Al_2(SO_4)_3/SiO_2$	hexane	91.0	1.0	50
	benzene	6.1	3.1	1700
reduced $CoMo/Al_2O_3$ [1)]	hexane	93.3	1.2	31
	benzene	4.3	5.6	—
reduced $NiMo/Al_2O_3$ [1)]	hexane	92.1	1.3	25
	benzene	6.4	4.2	—

1) Catalyst reduction pretreatment ; H_2 flow , 360℃-3h

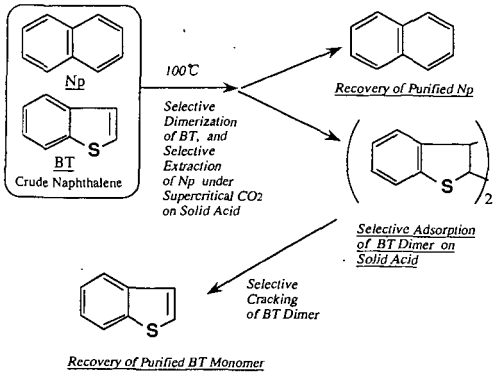

Fig 5 **Recovery Scheme of Purified Np and BT through Selective Dimerization of BT and Extraction of Np under Supercritical CO2 Conditions on Solid Acid Catalyst**

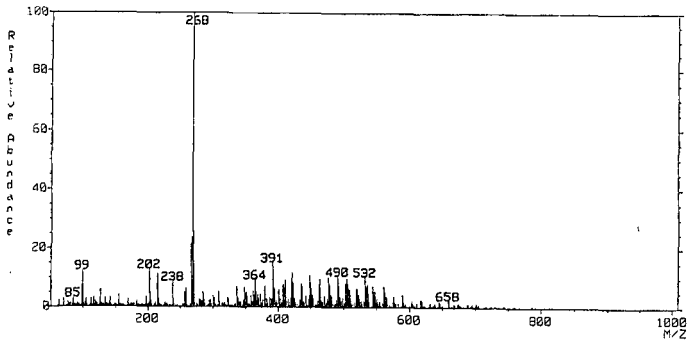

Fig6 FD-MS spectra of B.T oligomerization products conditions in atmospheric octane solution

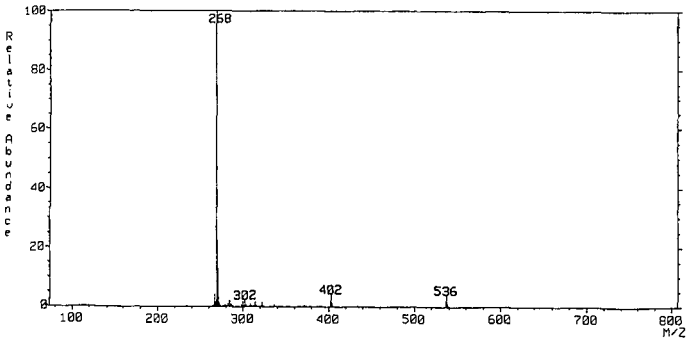

Fig 7 FD-MS spectrum of B.T oligomerization products under supercritical CO2 conditions